

# **Isotope Exchange for Gas-phase Acetic Acid and Ethanol at Aqueous Interfaces; A Study of Surface Reactions**

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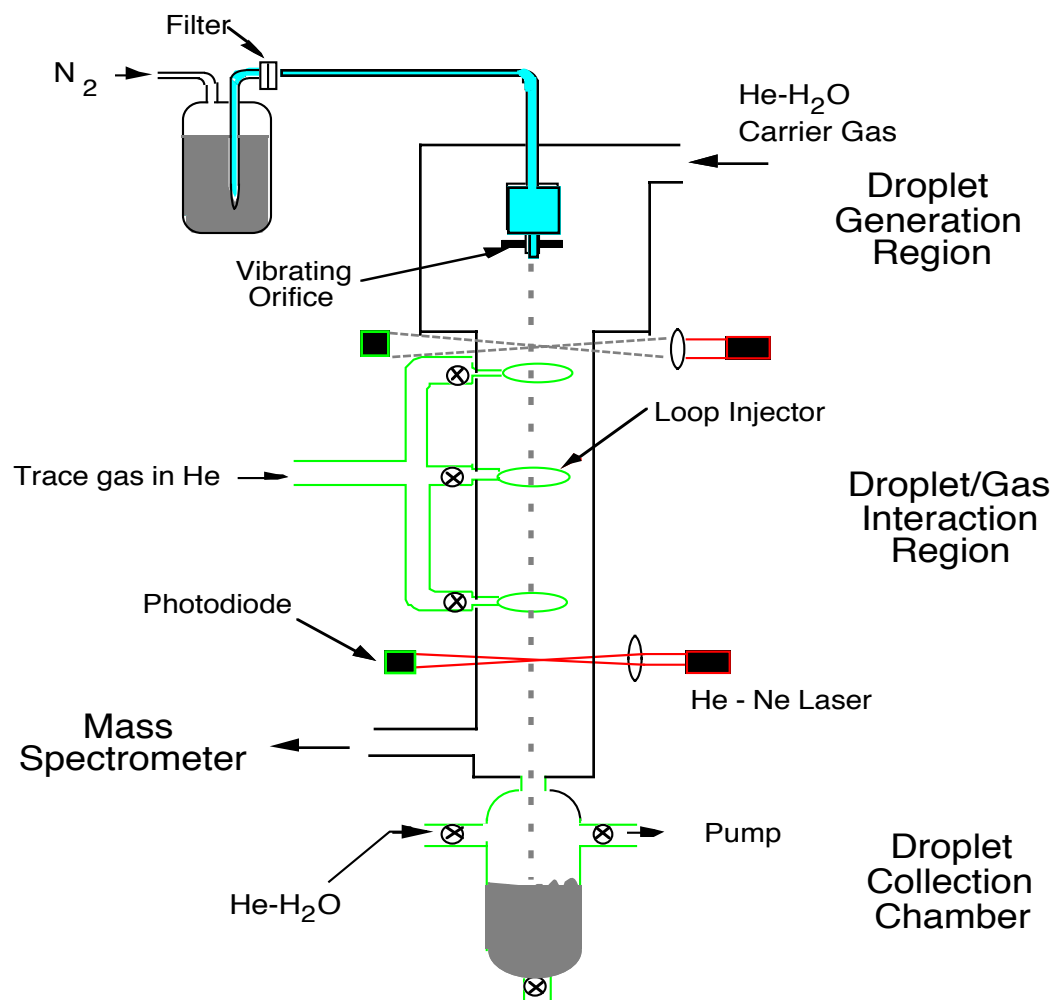
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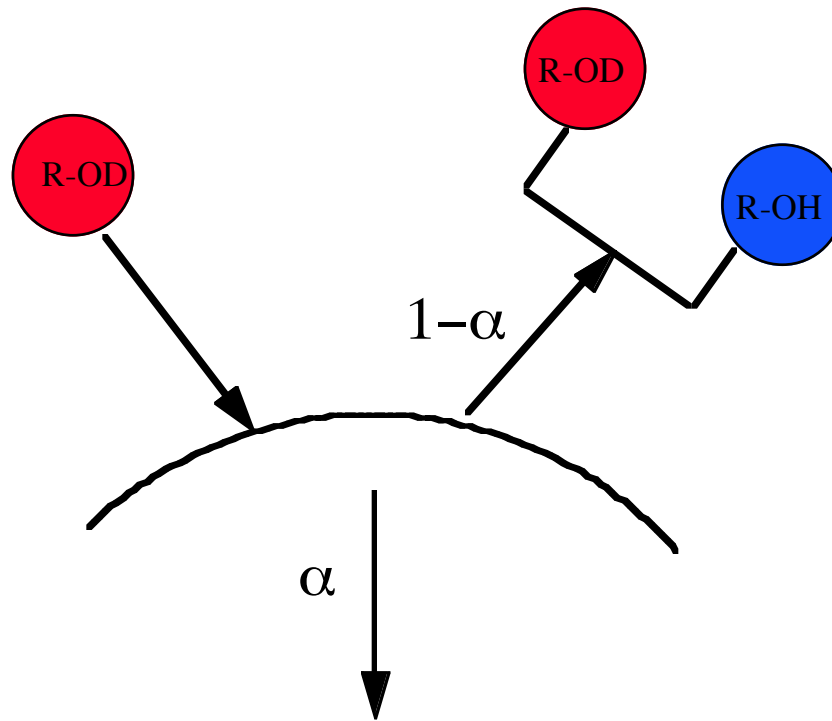
**Abstract.** Isotope exchange for deuterated gas-phase acetic acid and ethanol in contact with water ( $\text{H}_2\text{O}$ ) droplets was studied using a droplet train apparatus. In these experiments, the gas phase species interacts with liquid droplets and the loss of the species is monitored. The loss of the species may be due to the entry of the molecules into the bulk or to a reaction of the species at the gas-liquid interface; in this case isotope exchange. Studies were conducted as a function of pH in the range 0 to 14, droplet temperature in the range 291K to 263K and gas-liquid interaction time in the range 2 to 15 ms. For deuterated acetic acid the isotope exchange probability with water molecules at the interface is near unity. On the other hand, isotope exchange probability for ethanol with surface water molecules at pH 7 is much smaller ranging from 0.033 at 263K to 0.051 at 291K. Ethanol isotope exchange is both acid and base catalyzed. The exchange probability therefore increases both toward low and high pH and levels off to a plateau at pH 2 and 12 respectively. The maximum value of the isotope exchange probability at the plateau is significantly less than one. It ranges between 0.14 and 0.18 with no clear trend in temperature. Results are explained in terms of a kinetic model in which it is assumed that the surface adsorbed ethanol molecules are distributed between two distinct forms; a weakly adsorbed state, and a partially solvated state. Only the partially solvated molecules can interact with the near-surface ions in the interior of the liquid. A finite rate of entering the partially solvated state is responsible for the observed plateaus in isotope exchange at high and low pH. Parameters describing the gas uptake and isotope exchange processes are examined using two models to describe the surface species; surface nucleation and Gibbs surface excess.

Over the past several years it has become evident that several species of atmospheric importance are subject to reactions at the gas liquid interface.

**PURPOSE:** To obtain a clearer picture about the nature of chemical reactions at the gas-liquid interface

# Droplet Train Apparatus





The measured disappearance of deuterated species consists of two components:

1. Uptake of the species into bulk liquid governed by the mass accommodation coefficient ( $\alpha$ ) which is approximately the same for the two isotopes
2. Deuterium-hydrogen exchange at the gas-liquid interface.

$$\alpha = \frac{\text{no. of molecules entering the liquid phase}}{\text{no. of molecular collisions with the surface}}$$

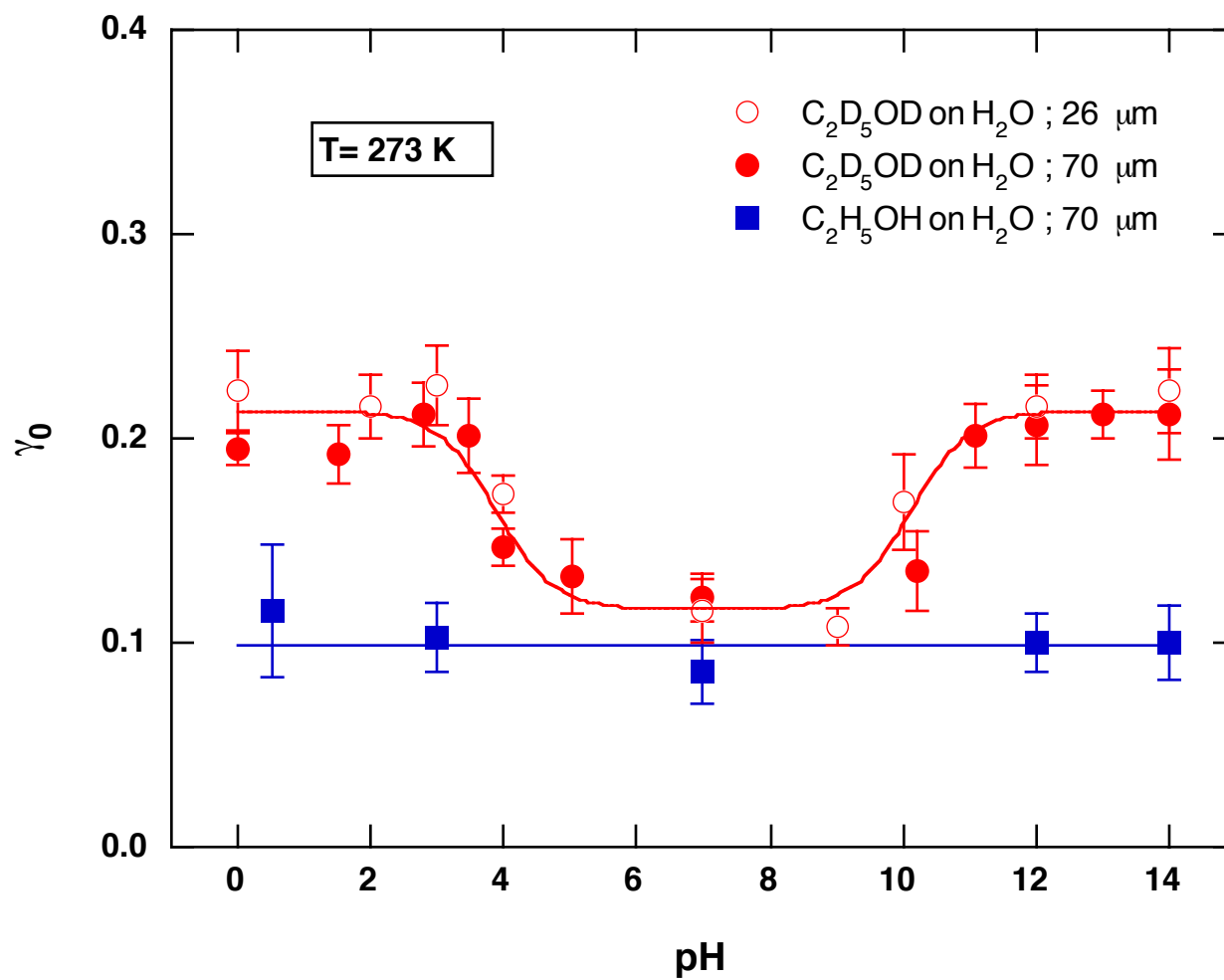
$$\gamma_0 = \frac{\text{no. of molecules disappearing from gas phase}}{\text{no. of molecular collisions with the surface}}$$

In the absence of surface reactions  $\alpha = \gamma_0$

With surface reactions  $\gamma_0 \geq \alpha$

# Gas Phase Diffusion-Corrected Uptake Coefficient as a Function of Droplet pH at

**T=273K**



## Observations:

- Enhanced disappearance of deuterated ethanol on water is due to D to H exchange on the surface.
- In acidic and basic pH regions,  $\gamma_o$  for deuterated ethanol reaches a plateau value of 0.2

## Conclusions:

1. Molecules at the interface are in two distinct forms; a weakly adsorbed state, and a partially solvated state.
2. Only the partially solvated molecules can interact with the near-surface ions in the interior of the liquid.
3. Formation of partially solvated state is the rate limiting step, causing observed plateau in  $\gamma_o$ .
4. Other surface reactions involving ions are likely to proceed similarly. e.g.  $\text{I}_2 + \text{Cl}^-(\text{aq}) \rightarrow \text{ICl} + \text{I}^-(\text{aq})$ .